

## Method for the treatment of paper surfaces

The present invention relates to a process for the treatment of paper surfaces, wherein the surface of the paper is coated with particles (composite particles) which are  
5 composed of polymer and finely divided inorganic solid, the weight average particle size of the finely divided inorganic solid being  $\leq 100$  nm.

The present invention also relates to a process for the treatment of paper surfaces, wherein the surface of the paper is treated with an aqueous dispersion which is  
10 obtainable by mixing an aqueous polymer dispersion with at least one dispersed, finely divided inorganic solid which has a weight average particle diameter of  $\leq 100$  nm.

Papers have a wide range of uses. Depending on their intended use, the papers must be capable of being readily written on or printed on (for example writing paper,  
15 newsprint, paper for journals, catalogs, books, etc.), must be absorbable (for example tissues, napkins, kitchen crepe paper and papers in the hygiene sector) or must be very strong, as, for example, in the case of banknote paper, Bible paper, kraft paper, capacitor paper or photographic paper.

20 Particularly in the case of the papers which can be written on and printed on and in the case of the very strong papers, the paper surfaces are frequently subjected to additional treatment steps for achieving the required properties. In particular, the paper surfaces are coated with paper coating slips or treated with paper sizes.

25 Paper coating slips substantially comprise a polymeric binder, one or more pigments and various further assistants. Through coating with paper coating slips, base papers acquire a strong, smooth white surface having improved printability.

The binders used in the paper coating slips are usually acrylate or styrene/butadiene  
30 copolymers. Corresponding paper coating slips are described, for example, in WO 97/00776, EP-A 1101425 or EP-A 1132521.

The paper sizes are as a rule nonpigmented binders, for example starches, proteins, rosin sizes and aqueous polymer dispersions and in particular starch-containing  
35 aqueous polymer dispersions, which are described, for example, in EP-A 307816, EP-A 735065, DE-A 3627494 and DE-A 10039388. As a result of the sizing, in particular the fiber structure is consolidated and hence the water resistance and the writability and printability are improved. Furthermore, the pigment and fillers are better fixed.

40 It is an object of the present invention to provide a novel process for the surface modification of paper.

We have found that this object is achieved by the processes defined at the outset.

5 In the context of this document, paper is to be understood as meaning a material which, according to DIN 6730 (August 1985), is sheet-like and substantially comprises fibers of predominantly vegetable origin and which is formed by draining a fiber suspension containing various assistants on a wire, the fiber felt thus obtained then being compacted and dried. Assistants used are, for example, fillers, dyes, pigments, binders, optical brighteners, retention aids, wetting agents, antifoams, preservatives,  
10 slime control agents, plasticizers, antiblocking agents, antistatic agents, water repellents, etc. known to a person skilled in the art. Depending on the basis weight achieved for the sheet-like material obtained, the term base paper (basis weight  $\leq 225 \text{ g/m}^2$ ) or raw board (basis weight  $> 225 \text{ g/m}^2$ ) is also used. Another customary term is cardboard, which, with a basis weight of from about 150 to  $600 \text{ g/m}^2$ , comprises  
15 both base paper grades and raw board grades. For reasons of simplicity, the term base paper below includes base paper, raw board and cardboard.

Frequently, the base paper is also treated by coating or is converted into the ready-to-use form. Coating of paper is understood as meaning the one-sided or two-sided  
20 coating of the paper with an aqueous coating slip substantially comprising pigments and binders. Depending on the type of coating slip, the coat thickness to be achieved or the paper grade to be produced, various coating methods are used for this purpose, for example the roll coating, knife coating, air brush or cast coating methods known to a person skilled in the art, which are followed in each case by a drying step. The papers  
25 thus treated are referred to as coated papers.

A further process for the treatment of papers comprises the treatment of the paper surfaces with sizes. The papers thus treated are referred to as sized papers.

30 The essential feature is that the novel processes are suitable both for base papers and for coated and sized papers.

In one embodiment, the composite particles are applied in the form of an aqueous composite particle dispersion to the paper surface (process 1).

35 Aqueous dispersions of composite particles are generally known. They are fluid systems which contain, as disperse phase present in disperse distribution and in aqueous dispersing medium, particles composed of a plurality of polymer balls consisting of entangled polymer chains, i.e. the polymer matrix, and finely divided

inorganic solid. The diameter of the composite particles is frequently from 30 to 5 000 nm.

Composite particles and processes for their preparation in the form of aqueous composite particle dispersions are known to a person skilled in the art and are disclosed, for example, in US-A 3,544,500, US-A 4,421,660, US-A 4,608,401, US-A 4,981,882, EP-A 104 498, EP-A 505 230, EP-A 572 128, GB-A 2 227 739, WO 0118081, WO 0129106 and in Long et al., Tianjin Daxue Xuebao 4 (1991), 10 to 14, Bourgeat-Lami et al., Die Angewandte Makromolekulare Chemie 242 (1996), 105 to 122, Paulke et al., Synthesis Studies of Paramagnetic Polystyrene Latex Particles in Scientific and Clinical Applications of Magnetic Carriers, pages 69 to 76, Plenum Press, New York, 1997, Armes et al., Advanced Materials 11 No. 5 (1999), 408 to 410.

For example, aqueous composite particle dispersions which were prepared according to the procedure disclosed in WO 03000760 are also suitable according to the invention. This process comprises dispersing at least one ethylenically unsaturated monomer in an aqueous medium and polymerizing by means of at least one free radical polymerization initiator in the presence of at least one dispersed, finely divided inorganic solid and at least one anionic, cationic and nonionic dispersant by the aqueous free radical emulsion polymerization method,

- a) a stable aqueous dispersion of the at least one inorganic solid being used, which dispersion, with an initial solids concentration of  $\geq 1\%$  by weight, based on the aqueous dispersion of the at least one inorganic solid, still contains more than 90% by weight of the originally dispersed solid in dispersed form one hour after its preparation and whose dispersed solid particles have a diameter of  $\leq 100$  nm,
- b) the disperse solid particles of the at least one inorganic solid having an electrophoretic mobility which differs from zero in an aqueous standard potassium chloride solution at a pH which corresponds to the pH of the aqueous reaction medium before the beginning of the addition of the dispersants,
- c) at least one anionic, cationic and nonionic dispersant being added to the aqueous solid particle dispersion before the beginning of the addition of the at least one ethylenically unsaturated monomer,
- d) thereafter from 0.01 to 30% by weight of the total amount of the at least one monomer being added to the aqueous solid particle dispersion and being polymerized to a conversion of at least 90%

and

- e) the remaining amount of the at least one monomer then being added continuously under polymerization conditions at the rate at which it is consumed.

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Suitable for this process are all those finely divided inorganic solids which form stable aqueous dispersions which, with an initial solids concentration of  $\geq 1\%$  by weight, based on the aqueous dispersion of the at least one inorganic solid, still contain more than 90% by weight of the originally dispersed solid in dispersed form one hour after  
10 their preparation without stirring or shaking and whose dispersed solid particles have a diameter of  $\leq 100$  nm and moreover have an electrophoretic mobility differing from zero at a pH which corresponds to the pH of the aqueous reaction medium before the beginning of the addition of the dispersants.

- 15 The quantitative determination of the initial solids concentration and of the solids concentration after one hour and the determination of the particle diameter are effected by the analytical ultracentrifuge method (in this context, cf. S.E. Harding et al., Analytical Ultracentrifugation in Biochemistry and Polymer Science, Royal Society of Chemistry, Cambridge, Great Britain 1992, Chapter 10, Analysis of Polymer  
20 Dispersions with an Eight-Cell-AUC-Multiplexer: High Resolution Particle Size Distribution and Density Gradient Techniques, W. Mächtle, pages 147 to 175). The values stated in the case of the particle diameters correspond to the  $d_{50}$  values.

- The method for the determination of the electrophoretic mobility is known to a person skilled in the art (cf. for example R.J. Hunter, Introduction to Modern Colloid Science, Section 8.4, pages 241 to 248, Oxford University Press, Oxford, 1993, and K. Oka and K. Furusawa, in Electrical Phenomena at Interfaces, Surfactant Science Series, Vol. 76, Section 8, pages 151 to 232, Marcel Dekker, New York, 1998). The electrophoretic mobility of the solid particles dispersed in aqueous reaction medium is determined by  
30 means of a commercial electrophoresis apparatus, for example the Zetasizer 3000 from Malvern Instruments Ltd., at 20°C and 1 bar (absolute). For this purpose, the aqueous solid particle dispersion is diluted with a pH-neutral 10 millimolar (mM) aqueous potassium chloride solution (standard potassium chloride solution) until the solid particle concentration is from about 50 to 100 mg/l. The adjustment of the test  
35 sample to the pH which the aqueous reaction medium has before the beginning of the addition of the dispersants is effected by means of the conventional inorganic acids, for example dilute hydrochloric acid or nitric acid, or bases, for example dilute sodium hydroxide solution or potassium hydroxide solution. The migration of the dispersed solid particles in the electric field is detected by means of the electrophoretic light  
40 scattering (cf. for example B.R. Ware and W.H. Flygare, Chem. Phys. Lett. 12 (1971),

81 to 85). The sign of the electrophoretic mobility is defined by the direction of migration of the dispersed solid particles, i.e. the electrophoretic mobility of the dispersed solid particles is positive if they migrate to the cathode and, on the other hand, is negative if they migrate to the anode.

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A suitable parameter for influencing or adjusting the electrophoretic mobility of dispersed solid particles in a certain environment is the pH of the aqueous reaction medium. By protonation or deprotonation of the dispersed solid particles, the electrophoretic mobility is changed in the positive direction in the acidic pH range (pH < 7) and in the negative direction in the alkaline range (pH > 7). The pH range suitable for the process disclosed in WO 03000760 is that within which a free radical aqueous emulsion polymerization can be carried out. This pH range is as a rule from pH 1 to 12, frequently from pH 1.5 to 11, often from pH 2 to 10.

15 The pH of the aqueous reaction medium can be adjusted by means of commercial acids, for example dilute hydrochloric, nitric or sulfuric acid, or bases, for example dilute sodium hydroxide solution or potassium hydroxide solution. It is frequently advantageous if a portion or the total amount of the amount of acid or base used for the pH adjustment is added to the aqueous reaction medium before the at least one finely divided inorganic solid.

What is important for the process disclosed according to WO 033000760 is that, when, under the abovementioned pH conditions, the dispersed solid particles

- 25 - have an electrophoretic mobility with a negative sign, from 0.01 to 10, preferably from 0.05 to 5, particularly preferably from 0.1 to 3, parts by weight of at least one cationic dispersant, from 0.01 to 100, preferably from 0.05 to 50, particularly preferably from 0.1 to 20, parts by weight of at least one nonionic dispersant and at least one anionic dispersant are used per 100 parts by weight of the at least one ethylenically unsaturated monomer, the amount of which anionic dispersant being such that the ratio of the number of equivalents of anionic dispersant to that of cationic dispersant is greater than 1, or
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- 35 - have an electrophoretic mobility with a positive sign, from 0.01 to 10, preferably from 0.05 to 5, particularly preferably from 0.1 to 3, parts by weight of at least one anionic dispersant, from 0.01 to 100, preferably from 0.05 to 50, particularly preferably from 0.01 to 20, parts by weight of at least one nonionic dispersant and at least one cationic dispersant are used per 100 parts by weight of the at least one ethylenically unsaturated monomer, the amount of which cationic dispersant

being such that the ratio of the number of equivalents of cationic dispersant to that of anionic dispersant is greater than 1.

5 The ratio of the number of equivalents of anionic dispersant to that of cationic dispersant is understood as meaning the ratio of the number of moles of the anionic dispersant, multiplied by the number of anionic groups contained per mole of the anionic dispersant, divided by the number of moles of the cationic dispersant used, multiplied by the number of cationic groups contained per mole of the cationic dispersant. The same applies to the ratio of the number of equivalents of cationic  
10 dispersant to that of anionic dispersant.

The total amount of the at least one anionic, cationic and nonionic dispersant used according to WO 03000760 can be initially taken in the aqueous solid dispersion. However, it is also possible initially to take only a portion of said dispersants in the  
15 aqueous solid dispersion and to add the remaining amounts continuously or batchwise during the free radical emulsion polymerization. However, it is essential to the process that the abovementioned ratio of the number of equivalents of anionic dispersant to that of cationic dispersant is maintained before or during the free radical emulsion polymerization, depending on the electrophoretic sign of the finely divided solid. If  
20 inorganic solid particles which have an electrophoretic mobility with a negative sign under the abovementioned pH conditions are used, the ratio of the number of equivalents of anionic dispersant to that of cationic dispersant must therefore be greater than 1 during the entire emulsion polymerization. In a corresponding manner, in the case of inorganic solids particles having an electrophoretic mobility with a positive  
25 sign, the ratio of the number of equivalents of cationic dispersant to that of anionic dispersant must be greater than 1 during the entire emulsion polymerization. It is advantageous if the ratios of the numbers of equivalents are  $\geq 2$ ,  $\geq 3$ ,  $\geq 4$ ,  $\geq 5$ ,  $\geq 6$ ,  $\geq 7$  or  $\geq 10$ , the ratios of the numbers of equivalents particularly advantageously being from 2 to 5.

30 A further process for the treatment of paper surfaces comprises treating the surface of the paper with an aqueous dispersion which by mixing an aqueous polymer dispersion with at least one dispersed, finely divided organic solid which has a weight average particle diameter of  $< 100$  nm (process 2).

35 Aqueous polymer dispersions are generally known. They are fluid systems which contain, present as the disperse phase dispersed in an aqueous dispersing medium, polymer balls consisting of a plurality of entangled polymer chains, i.e. the polymer matrix or polymer particle. The diameter of the polymer particles is frequently from 10  
40 to 5 000 nm.

The preparation of an aqueous polymer dispersion is effected, for example, by means of free radical aqueous emulsion polymerization. The procedure for a free radical aqueous emulsion polymerization of ethylenically unsaturated monomers has been widely described and is therefore sufficiently well known to a person skilled in the art [cf. for example Encyclopedia of Polymer Science and Engineering, Vol. 8, pages 659 to 677, John Wiley & Sons, Inc., 1987; D.C. Blackley, Emulsion Polymerisation, pages 155 to 465, Applied Science Publishers, Ltd., Essex, 1975; D.C. Blackley, Polymer Latexes, 2<sup>nd</sup> Edition, Vol. 1, pages 33 to 415, Chapman & Hall, 1997; H. Warson, The Applications of Synthetic Resin Emulsions, pages 49 to 244, Ernest Benn, Ltd., London, 1972; D. Diederich, Chemie in unserer Zeit 24 (1990), 135 to 142, Verlag Chemie, Weinheim; J. Piirma, Emulsion Polymerisation, pages 1 to 287, Academic Press, 1982; F. Hölscher, Dispersionen synthetischer Hochpolymerer, pages 1 to 160, Springer-Verlag, Berlin, 1969 and DE-A 40 03 422]. It is usually carried out by dispersing the ethylenically unsaturated monomers in the presence of dispersants in an aqueous medium and polymerizing them by means of at least one free radical polymerization initiator. The process disclosed in WO 03000760 differs from this procedure only in an additional presence of at least one finely divided inorganic solid which has an electrophoretic mobility differing from zero and in the use of a special dispersant combination during the polymerization.

Metals, metal compounds, such as metal oxides and metal salts, but also semimetal and nonmetal compounds, are suitable finely divided inorganic solids which can be used for both novel processes. Noble metal colloids, for example palladium, silver, ruthenium, platinum, gold and rhodium, and alloys containing them can be used as finely divided metal powders. Examples of finely divided metal oxides are titanium dioxide (for example commercially available as Hombitec<sup>®</sup> grades from Sachtleben Chemie GmbH), zirconium(IV) oxide, tin(II) oxide, tin(IV) oxide (for example commercially available as Nyacol<sup>®</sup> SN grades from Akzo-Nobel), alumina (for example commercially available as Nyacol<sup>®</sup> AL grades from Akzo-Nobel), barium oxide, magnesium oxide, various iron oxides, such as iron(II) oxide (wuestite), iron(III) oxide (hematite) and iron(II/III) oxide (magnetite), chromium(III) oxide, antimony(III) oxide, bismuth(III) oxide, zinc oxide (for example commercially available as Sachtotec<sup>®</sup> grades from Sachtleben Chemie GmbH), nickel(II) oxide, nickel(III) oxide, cobalt(II) oxide, cobalt(III) oxide, copper(II) oxide, yttrium(III) oxide (for example commercially available as Nyacol<sup>®</sup> YTTRIA grades from Akzo-Nobel), cerium(IV) oxide (for example commercially available as Nyacol<sup>®</sup> CEO2 grades from Akzo-Nobel), in amorphous form and/or in their various crystal modifications, and the hydrated oxides thereof, for example hydrated titanium(IV) oxide, hydrated zirconium(IV) oxide, hydrated aluminum oxide (for example commercially available as Disperal<sup>®</sup> grades from Condea-Chemie

GmbH) and hydrated iron(III) oxide, in amorphous form and/or in their different crystal modifications. The following amorphous metal salts and metal salts present in their different crystal structures can in principle be used in the novel process: sulfides, such as iron(II) sulfide, iron(III) sulfide, iron(II) disulfide (pyrite), tin(II) sulfide, tin(IV) sulfide, 5 mercury(II) sulfide, cadmium(II) sulfide, zinc sulfide, copper(II) sulfide, silver sulfide, nickel(II) sulfide, cobalt(II) sulfide, cobalt(III) sulfide, manganese(II) sulfide, chromium(III) sulfide, titanium(II) sulfide, titanium(III) sulfide, titanium(IV) sulfide, zirconium(IV) sulfide, antimony(III) sulfide and bismuth(II) sulfide, hydroxides, such as tin(II) hydroxide, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, 10 barium hydroxide, zinc hydroxide, iron(II) hydroxide and iron(III) hydroxide, sulfates, such as calcium sulfate, strontium sulfate, barium sulfate and lead(IV) sulfate, carbonates, such as lithium carbonate, magnesium carbonate, calcium carbonate, zinc carbonate, zirconium(IV) carbonate, iron(II) carbonate, and iron(III) carbonate, orthophosphates, such as lithium orthophosphate, calcium orthophosphate, zinc 15 orthophosphate, magnesium orthophosphate, aluminum orthophosphate, tin(III) orthophosphate, iron(II) orthophosphate and iron(III) orthophosphate, metaphosphates, such as lithium metaphosphate, calcium metaphosphate and aluminum metaphosphate, pyrophosphates, such as magnesium pyrophosphate, calcium pyrophosphate, zinc pyrophosphate, iron(III) pyrophosphate and tin(II) pyrophosphate, 20 ammonium phosphates, such as magnesium ammonium phosphate and zinc ammonium phosphate, hydroxyapatite  $[\text{Ca}_5\{(\text{PO}_4)_3\text{OH}\}]$ , orthosilicates, such as lithium orthosilicate, calcium/magnesium orthosilicate, aluminum orthosilicate, iron(II) orthosilicate, iron(III) orthosilicate, magnesium orthosilicate, zinc orthosilicate, zirconium(III) orthosilicate and zirconium(IV) orthosilicate, metasilicates, such as lithium 25 metasilicate, calcium/magnesium metasilicate, calcium metasilicate, magnesium metasilicate and zinc metasilicate, sheet silicates, such as sodium aluminum silicate and sodium magnesium silicate, in particular in spontaneously delaminating form, for example Optigel® SH (grade from Südchemie AG), Saponit® SKS-20 and Hektorit® SKS 21 (grades from Hoechst AG) and Laponite® RD and Laponite® GS (grades from 30 Laporte Industries Ltd.), aluminates, such as lithium aluminate, calcium aluminate and zinc aluminate, borates, such as magnesium metaborate and magnesium orthoborate, oxalates, such as calcium oxalate, zirconium(IV) oxalate, magnesium oxalate, zinc oxalate and aluminum oxalate, tartrates, such as calcium tartrate, acetylacetonates, such as aluminum acetylacetonate and iron(III) acetylacetonate, salicylates, such as 35 aluminum salicylate, citrates, such as calcium citrate, iron(II) citrate and zinc citrate, palmitates, such as aluminum palmitate, calcium palmitate and magnesium palmitate, stearates, such as aluminum stearate, calcium stearate, magnesium stearate and zinc stearate, laurates, such as calcium laurate, linoleates, such as calcium linoleate, oleates, such as calcium oleate, iron(II) oleate or zinc oleate.



- Amorphous silica and/or silica present in different crystal structures may be mentioned as important semimetal compounds which may be used according to the invention. Silica suitable according to the invention is commercially available and can be obtained, for example, as Aerosil® (grade from Degussa AG), Levasil® (grade from Bayer AG), Ludox® (grade from DuPont), Nyacol® and Bindzil® (grades from Akzo-Nobel) and Snowtex® (grade from Nissan Chemical Industries, Ltd.). Nonmetal compounds suitable according to the invention are, for example, colloidal graphite or diamond.
- 10 Particularly suitable finely divided inorganic solids are those whose solubility in water at 20°C and 1 bar (absolute) is  $\leq 1$ , preferably  $\leq 0.1$ , in particular  $\leq 0.01$ , g/l. Compounds selected from the group consisting of silica, alumina, tin(IV) oxide, yttrium(III) oxide, cerium(IV) oxide, hydrated aluminum oxide, calcium carbonate, magnesium carbonate, calcium orthophosphate, magnesium orthophosphate, calcium metaphosphate, magnesium metaphosphate, calcium pyrophosphate, magnesium pyrophosphate, iron(II) oxide, iron(III) oxide, iron(II/III) oxide, titanium dioxide, hydroxylapatite, zinc oxide and zinc sulfide are particularly preferred. Silica sols which have an electrophoretic mobility with a negative sign are particularly preferred.
- 20 The commercially available compounds of the Aerosil®, Levasil®, Ludox®, Nyacol® and Bindzil® grades (silica), Disperal® grades (hydrated aluminum oxide), Nyacol® AL grades (alumina), Hombitec® grades (titanium dioxide), Nyacol® SN grades (tin(IV) oxide), Nyacol® YTTRIA grades (yttrium(III) oxide), Nyacol® CEO2 grades (cerium(IV) oxide) and Sachtotec® grades (zinc oxide) can also advantageously be used in the novel processes.
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- The finely divided inorganic solids which can be used in the novel processes are such that the solid particles dispersed in the aqueous reaction medium have a particle diameter of  $\leq 100$  nm. Those finely divided inorganic solids whose disperse particles have a particle diameter of  $> 0$  nm but  $\leq 90$  nm,  $\leq 80$  nm,  $\leq 70$  nm,  $\leq 60$  nm,  $\leq 50$  nm,  $\leq 40$  nm,  $\leq 30$  nm,  $\leq 20$  nm or  $\leq 10$  nm and all values in between are successfully used. Finely divided inorganic solids which have a particle diameter of  $\leq 50$  nm are advantageously used. The particle diameters are determined using the analytical ultracentrifuge method.
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- 35 The finely divided solids are obtainable by a procedure known in principle to a person skilled in the art and are obtained, for example, by precipitation reactions or chemical reactions in the gas phase (in this context, cf. E. Matijevic, Chem. Mater. 5 (1993), 412 to 426; Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 23, pages 583 to 660, Verlag Chemie, Weinheim, 1992; D.F. Evans, H. Wennerström in The Colloidal
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Domain, pages 363 to 405, Verlag Chemie, Weinheim, 1994, and R.J. Hunter in Foundations of Colloid Science, Vol. I, pages 10 to 17, Clarendon Press, Oxford, 1991).

- 5 The stable solid dispersion is frequently prepared directly during the synthesis of the finely divided inorganic solids in an aqueous medium or alternatively by dispersing the finely divided inorganic solid in the aqueous medium. Depending on the method of preparation of the finely divided inorganic solids, this is effected either directly, for example in the case of precipitated or pyrogenic silica, alumina, etc., or with the aid of  
10 suitable auxiliary units, for example dispersers or ultrasonic sonotrodes.

However, only those finely divided inorganic solids whose aqueous solid dispersion, with an initial solids concentration of  $\geq 1\%$  by weight, based on the aqueous dispersion of the finely divided inorganic solid, still contains more than 90% by weight of the  
15 originally dispersed solid in dispersed form one hour after their preparation or as a result of stirring up or shaking up the sedimented solids, without further stirring or shaking, and whose dispersed solid particles have a diameter of  $\leq 100$  nm are suitable according to the invention. Initial solids concentrations of  $\leq 60\%$  by weight are usual. Advantageously, however, initial solids concentrations of  $\leq 55$ ,  $\leq 50$ ,  $\leq 45$ ,  $\leq 40$ ,  $\leq 35$ ,  
20  $\leq 30$ ,  $\leq 25$ ,  $\leq 20$ ,  $\leq 15$  or  $\leq 10\%$  by weight and  $\geq 2$ ,  $\geq 3$ ,  $\geq 4$  or  $\geq 5\%$  by weight and all values in between, based in each case on the aqueous dispersion of finely divided inorganic solid, can also be used. According to the invention, from 1 to 1 000, as a rule from 5 to 300, frequently from 10 to 200, parts by weight of the at least one finely divided inorganic solid are used per 100 parts by weight of the at least one ethylenically  
25 unsaturated monomer in the preparation of aqueous composite particle dispersions (process 1) or 100 parts by weight of dispersion polymer (process 2).

Both in the preparation of the aqueous composite particle dispersion and in the preparation of the aqueous polymer dispersion and in the mixing thereof with the finely  
30 divided inorganic solid, dispersants are present which keep both the finely divided inorganic solid particles and the monomer droplets, and the composite particles formed or the mixture of the polymer particles and of the finely divided inorganic solid, dispersed in the aqueous phase and thus ensure the stability of the aqueous dispersions produced. Considerable dispersions are both the protective colloids usually  
35 used for carrying out free radical aqueous emulsion polymerization and emulsifiers.

A detailed description of suitable protective colloids appears in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 411 to 420.

Suitable neutral protective colloids are, for example, polyvinyl alcohols, polyalkylene glycols, cellulose derivatives, starch derivatives and gelatin derivatives.

5     Suitable anionic protective colloids, i.e. protective colloids whose component having a dispersing effect has at least one negative electrical charge, are, for example, polyacrylic acids and polymethacrylic acids and the alkali metal salts thereof, copolymers containing acrylic acid, methacrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, 4-styrenesulfonic acid and/or maleic anhydride, and the  
10     alkali metal salts thereof, and alkali metal salts of sulfonic acids of high molecular weight compounds, for example polystyrene.

15     Suitable cationic protective colloids, i.e. protective colloids whose component having a dispersing effect has at least one positive electrical charge, are, for example, the homo- and copolymers containing those derivatives of N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylcarbazole, 1-vinylimidazole, 2-vinylimidazole, 2-vinylpyridine, 4-vinylpyridine, acrylamide, methacrylamide, amino-carrying acrylates, methacrylates, acrylamides and/or methacrylamides which are protonated and/or alkylated on the nitrogen.

20     Of course, mixtures of emulsifiers and/or protective colloids may also be used. Frequently, exclusively emulsifiers whose relative molecular weights, in contrast to the protective colloids, are usually below 1 500 are used as dispersants. Of course, where mixtures of surface-active substances are used, the individual components must be compatible with one another, which can be checked by means of a few preliminary  
25     experiments in case of doubt. An overview of suitable emulsifiers appears in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 192 to 208.

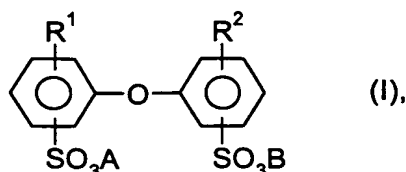
30     Customary nonionic emulsifiers are, for example, ethoxylated mono-, di- and trialkylphenols (degree of ethoxylation: from 3 to 50, alkyl radical: C<sub>4</sub> to C<sub>12</sub>) and ethoxylated fatty alcohols (degree of ethoxylation: from 3 to 80; alkyl radical: C<sub>8</sub> to C<sub>36</sub>). Examples of these are Lutensol® A grades (C<sub>12</sub>C<sub>14</sub>-fatty alcohol ethoxylates, degree of ethoxylation: from 3 to 8), Lutensol® AO grades (C<sub>13</sub>C<sub>15</sub>-oxo alcohol ethoxylates, degree of ethoxylation: from 3 to 30), Lutensol® AT grades (C<sub>16</sub>C<sub>18</sub>-fatty alcohol  
35     ethoxylates, degree of ethoxylation: from 11 to 80), Lutensol® ON grades (C<sub>10</sub>-oxo alcohol ethoxylates, degree of ethoxylation: from 3 to 11) and the Lutensol® TO grades (C<sub>13</sub>-oxo alcohol ethoxylates, degree of ethoxylation: from 3 to 20) from BASF AG.

40     Conventional anionic emulsifiers are, for example, alkali metal and ammonium salts of alkyl sulfates (alkyl radical: C<sub>8</sub> to C<sub>12</sub>), of sulfuric monoesters of ethoxylated alkanols

(degree of ethoxylation: from 4 to 30, alkyl radical: C<sub>12</sub> to C<sub>18</sub>) and ethoxylated alkylphenols (degree of ethoxylation: from 3 to 50, alkyl radical: C<sub>4</sub> to C<sub>12</sub>), of alkanesulfonic acids (alkyl radical: C<sub>12</sub> to C<sub>18</sub>) and of alkylarylsulfonic acids (alkyl radical: C<sub>9</sub> to C<sub>18</sub>).

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Compounds of the formula I



where R<sup>1</sup> and R<sup>2</sup> are H or C<sub>4</sub>- to C<sub>24</sub>-alkyl and are not simultaneously H, and A and B may be alkali metal ions and/or ammonium ions, have also proven to be further anionic emulsifiers. In formula I, R<sup>1</sup> and R<sup>2</sup> are preferably linear or branched alkyl of 6 to 18, in particular 6, 12 or 16, carbon atoms or -H, R<sup>1</sup> and R<sup>2</sup> not both simultaneously being H. A and B are preferably sodium, potassium or ammonium, sodium being particularly preferred. Compounds I in which A and B are sodium, R<sup>1</sup> is branched alkyl having 12 carbon atoms and R<sup>2</sup> is H or R<sup>1</sup> are particularly advantageous. Industrial mixtures which contain from 50 to 90% by weight of the monoalkylated products, for example Dowfax<sup>®</sup> 2A1 (brand of Dow Chemical Company), are frequently used. The compounds I are generally known, for example from US-A 4 269 749, and are commercially available.

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Suitable cationic emulsifiers are as a rule primary, secondary, tertiary or quaternary ammonium salts, alkanolammonium salts, pyridinium salts, imidazolinium salts, oxazolinium salts, morpholinium salts, thiazolinium salts and salts of amine oxides, quinolinium salts, isoquinolinium salts, tropylium salts, sulfonium salts and phosphonium salts having a C<sub>6</sub>- to C<sub>18</sub>-alkyl, C<sub>6</sub>- to C<sub>18</sub>-aralkyl or a heterocyclic radical. Examples are dodecylammonium acetate or the corresponding hydrochloride, the chlorides or acetates of the various 2-(N,N,N-trimethylammonium)ethylparaffinic acid esters, N-cetylpyridinium chloride, N-laurylpyridinium sulfate and N-cetyl-N,N,N-trimethylammonium bromide, N-dodecyl-N,N,N-trimethylammonium bromide, N-octyl-N,N,N-trimethylammonium bromide, N,N-distearyl-N,N-dimethylammonium chloride and the Gemini surfactant N,N'-(lauryldimethyl)ethylenediamine dibromide. Numerous further examples appear in H. Stache, Tensid-Taschenbuch, Carl-Hanser-Verlag, Munich, Vienna, 1981 and in McCutcheon's, Emulsifiers & Detergents, MC Publishing Company, Glen Rock, 1989.

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The aqueous dispersions which can be used according to the invention in processes 1 and 2 contain, as a rule, from 0.1 to 10, often from 0.5 to 7.0, frequently from 1.0 to 5.0,

% by weight, based in each case on the aqueous dispersion, of dispersant. Emulsifiers are preferably used.

Suitable ethylenically unsaturated monomers for the preparation of the composite particles which can be used according to the invention (process 1) and the dispersion polymer used according to the invention (process 2) are, inter alia, in particular monomers which can be subjected to free radical polymerization in a simple manner, such as ethylene, vinylaromatic monomers, such as styrene,  $\alpha$ -methylstyrene, o-chlorostyrene or vinyltoluenes, esters of vinyl alcohol and monocarboxylic acids of 1 to 18 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate and vinyl stearate, esters of  $\alpha,\beta$ -monoethylenically unsaturated mono- and dicarboxylic acids preferably of 3 to 6 carbon atoms, in particular acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid, with alkanols of in general 1 to 12, preferably 1 to 8, in particular 1 to 4, carbon atoms, in particular methyl, ethyl, n-butyl, isobutyl and 2-ethylhexyl acrylate and methacrylate, dimethyl maleate or di-n-butyl maleate, nitriles of  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acids, such as acrylonitrile, and conjugated  $C_{4-8}$ -dienes, such as 1,3-butadiene and isoprene. Said monomers are, as a rule, the main monomers, which together usually account for an amount of  $\geq 50$ ,  $\geq 80$  or  $\geq 90\%$  by weight, based on the total amount of the monomers to be polymerized by the novel process. As a rule, these monomers have only moderate to low solubility in water under standard conditions [20°C, 1 bar (absolute)].

Monomers which usually increase the internal strength of the films of the polymer matrix generally have at least one epoxy, hydroxyl, N-methylol or carbonyl group, or at least two nonconjugated ethylenically unsaturated double bonds. Examples of these are monomers having two vinyl radicals, monomers having two vinylidene radicals and monomers having two alkenyl radicals. Particularly advantageous are the diesters of dihydric alcohols with  $\alpha,\beta$ -monoethylenically unsaturated monocarboxylic acids, among which acrylic and methacrylic acid are preferred. Examples of such monomers having two nonconjugated ethylenically unsaturated double bonds are alkylene glycol diacrylates and dimethacrylates, such as ethylene glycol diacrylate, 1,2-propylene glycol diacrylate, 1,3-propylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylates and ethylene glycol dimethacrylate, 1,2-propylene glycol dimethacrylate, 1,3-propylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate or 1,4-butylene glycol dimethacrylate, and divinylbenzene, vinyl methacrylate, vinyl acrylate, allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, methylenebisacrylamide, cyclopentadienyl acrylate, triallyl cyanurate or triallyl isocyanurate. Also of particular importance in this context are the  $C_1$ - $C_8$ -hydroxyalkyl methacrylates and acrylates, such as n-hydroxyethyl, n-hydroxypropyl or n-hydroxybutyl acrylate and methacrylate, and compounds such as diacetoneacrylamide

and acetylacetoxyethyl acrylate or methacrylate. According to the invention, the abovementioned monomers are incorporated in the form of polymerized units in amounts of up to 5% by weight, based on the total amount of the monomers to be polymerized.

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Monomers containing siloxane groups, such as the vinyltrialkoxysilanes, for example vinyltrimethoxysilane, alkylvinylalkoxysilanes, acryloyloxyalkyltrialkoxysilanes or methacryloyloxyalkyltrialkoxysilanes, for example acryloyloxyethyltrimethoxysilane, methacryloyloxyethyltrimethoxysilane, acryloyloxypropyltrimethoxysilane or methacryloyloxypropyltrimethoxysilane, can optionally also be used. These monomers are used in amounts of up to 2, frequently from 0.01 to 1, often from 0.05 to 0.5, % by weight, based in each case on the total amount of monomers.

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Those ethylenically unsaturated monomers A which contain at least one acid group and/or the corresponding anion thereof or those ethylenically unsaturated monomers B which contain at least one amino, amido, ureido or N-heterocyclic group and/or the ammonium derivatives thereof which are protonated or alkylated on the nitrogen may additionally be used as monomers. The amount of monomers A or monomers B is up to 10, often from 0.1 to 7, frequently from 0.2 to 5, % by weight, based on the total amount of monomers.

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Ethylenically unsaturated monomers having at least one acid group are used as monomers A. The acid group may be, for example, a carboxyl, sulfo, sulfuric acid, phosphoric acid and/or phosphonic acid group. Examples of monomers A are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, 4-styrenesulfonic acid, 2-methacryloyloxyethylsulfonic acid, vinylsulfonic acid and vinylphosphonic acid and phosphoric monoesters of n-hydroxyalkyl acrylates and n-hydroxyalkyl methacrylates, for example phosphoric monoesters of hydroxyethyl acrylate, n-hydroxypropyl acrylate, n-hydroxybutyl acrylate and hydroxyethyl methacrylate, n-hydroxypropyl methacrylate and n-hydroxybutyl methacrylate.

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According to the invention, however, it is also possible to use the ammonium and alkali metal salts of the abovementioned ethylenically unsaturated monomers having at least one acid group. Sodium and potassium are particularly preferred as the alkali metal. Examples here are the ammonium, sodium and potassium salts of acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, 4-styrenesulfonic acid, 2-methacryloyloxyethylsulfonic acid, vinylsulfonic acid and vinylphosphonic acid and the mono- and diammonium, mono- and disodium and mono- and dipotassium salts of the phosphoric monoesters of hydroxyethyl acrylate, n-hydroxypropyl acrylate, n-hydroxybutyl acrylate and hydroxyethyl methacrylate, n-hydroxypropyl methacrylate or n-hydroxybutyl methacrylate.

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Acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, 4-styrenesulfonic acid, 2-methacryloyloxyethylsulfonic acid, vinylsulfonic acid and vinylphosphonic acid are preferably used.

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Ethylenically unsaturated monomers which contain at least one amino, amido, ureido or N-heterocyclic group and/or the ammonium derivatives thereof which are protonated or alkylated on the nitrogen are used as monomers B.

- 10 Examples of monomers B which contain at least one amino group are 2-aminoethyl acrylate, 2-aminoethyl methacrylate, 3-aminopropyl acrylate, 3-aminopropyl methacrylate, 4-amino-n-butyl acrylate, 4-amino-n-butyl methacrylate, 2-(N-methylamino)ethyl acrylate, 2-(N-methylamino)ethyl methacrylate, 2-(N-ethylamino)ethyl acrylate, 2-(N-ethylamino)ethyl methacrylate, 2-(N-n-propylamino)ethyl acrylate, 2-(N-n-propylamino)ethyl methacrylate, 2-(N-isopropylamino)ethyl acrylate, 2-(N-isopropylamino)ethyl methacrylate, 2-(N-tert-butylamino)ethyl acrylate, 2-(N-tert-butylamino)ethyl methacrylate (for example commercially available as Norsocryl<sup>®</sup> TBAEMA from Elf Atochem), 2-(N,N-dimethylamino)ethyl acrylate (for example commercially available as Norsocryl<sup>®</sup> ADAME from Elf Atochem), 2-(N,N-dimethylamino)ethyl methacrylate (for example commercially available as Norsocryl<sup>®</sup> MADAME from Elf Atochem), 2-(N,N-diethylamino)ethyl acrylate, 2-(N,N-diethylamino)ethyl methacrylate, 2-(N,N-di-n-propylamino)ethyl acrylate, 2-(N,N-di-n-propylamino)ethyl methacrylate, 2-(N,N-diisopropylamino)ethyl acrylate, 2-(N,N-diisopropylamino)ethyl methacrylate, 3-(N-methylamino)propyl acrylate, 3-(N-methylamino)propyl methacrylate, 3-(N-ethylamino)propyl acrylate, 3-(N-ethylamino)propyl methacrylate, 3-(N-n-propylamino)propyl acrylate, 3-(N-n-propylamino)propyl methacrylate, 3-(N-isopropylamino)propyl acrylate, 3-(N-isopropylamino)propyl methacrylate, 3-(N-tert-butylamino)propyl acrylate, 3-(N-tert-butylamino)propyl methacrylate, 3-(N,N-dimethylamino)propyl acrylate, 3-(N,N-dimethylamino)propyl methacrylate, 3-(N,N-diethylamino)propyl acrylate, 3-(N,N-diethylamino)propyl methacrylate, 3-(N,N-di-n-propylamino)propyl acrylate, 3-(N,N-di-n-propylamino)propyl methacrylate, 3-(N,N-diisopropylamino)propyl acrylate and 3-(N,N-diisopropylamino)propyl methacrylate.

- 35 Examples of monomers B which contain at least one amido group are acrylamide, methacrylamide, N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide, N-n-propylacrylamide, N-n-propylmethacrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, N-tert-butylacrylamide, N-tert-butylmethacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N,N-diethylacrylamide, N,N-diethylmethacrylamide, N,N-di-n-propylacrylamide, N,N-di-n-
- 40

- propylmethacrylamide, N,N-diisopropylacrylamide, N,N-diisopropylmethacrylamide, N,N-di-n-butylacrylamide, N,N-di-n-butylmethacrylamide, N-(3-N',N'-dimethylaminopropyl)methacrylamide, diacetoneacrylamide, N,N'-methylenebisacrylamide, N-(diphenylmethyl)acrylamide, N-cyclohexylacrylamide, but  
 5 also N-vinylpyrrolidone and N-vinylcaprolactam.

Examples of monomers B which contain at least one ureido group are N,N'-divinylethyleneurea and 2-(1-imidazolin-2-onyl)ethyl methacrylate (for example commercially available as Norsocryl® 100 from Elf Atochem).

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Examples of monomers B which contain at least one N-heterocyclic group are 2-vinylpyridine, 4-vinylpyridine, 1-vinylimidazole, 2-vinylimidazole and N-vinylcarbazole.

- The following compounds are preferably used: 2-vinylpyridine, 4-vinylpyridine, 2-vinylimidazole, 2-(N,N-dimethylamino)ethyl acrylate, 2-(N,N-dimethylamino)ethyl methacrylate, 2-(N,N-diethylamino)ethyl acrylate, 2-(N,N-diethylamino)ethyl methacrylate, 2-(N-tert-butylamino)ethyl methacrylate, N-(3-N',N'-dimethylaminopropyl)methacrylamide and 2-(1-imidazolin-2-onyl)ethyl methacrylate...

- 20 Depending on the pH of the aqueous reaction medium, a part or the total amount of the abovementioned nitrogen-containing monomers B may be present in the quaternary ammonium form protonated on the nitrogen.

- Examples of monomers B which have a quaternary alkylammonium structure on the  
 25 nitrogen are 2-(N,N,N-trimethylammonium)ethyl acrylate chloride (for example commercially available as Norsocryl® ADAMQUAT MC 80 from Elf Atochem), 2-(N,N,N-trimethylammonium)ethyl methacrylate chloride (for example commercially available as Norsocryl® MADQUAT MC 75 from Elf Atochem), 2-(N-methyl-N,N-diethylammonium)ethyl acrylate chloride, 2-(N-methyl-N,N-diethylammonium)ethyl  
 30 methacrylate chloride, 2-(N-methyl-N,N-dipropylammonium)ethyl acrylate chloride, 2-(N-methyl-N,N-dipropylammonium)ethyl methacrylate, 2-(N-benzyl-N,N-dimethylammonium)ethyl acrylate chloride (for example commercially available as Norsocryl® ADAMQUAT BZ 80 from Elf Atochem), 2-(N-benzyl-N,N-dimethylammonium)ethyl methacrylate chloride (for example commercially available as  
 35 Norsocryl® MADQUAT BZ 75 from Elf Atochem), 2-(N-benzyl-N,N-diethylammonium)ethyl acrylate chloride, 2-(N-benzyl-N,N-diethylammonium)ethyl methacrylate chloride, 2-(N-benzyl-N,N-dipropylammonium)ethyl acrylate chloride, 2-(N-benzyl-N,N-dipropylammonium)ethyl methacrylate chloride, 3-(N,N,N-trimethylammonium)propyl acrylate chloride, 3-(N,N,N-trimethylammonium)propyl  
 40 methacrylate chloride, 3-(N-methyl-N,N-diethylammonium)propyl acrylate chloride, 3-



(N-methyl-N,N-diethylammonium)propyl methacrylate chloride, 3-(N-methyl-N,N-dipropylammonium)propyl acrylate chloride, 3-(N-methyl-N,N-dipropylammonium)propyl methacrylate chloride, 3-(N-benzyl-N,N-dimethylammonium)propyl acrylate chloride, 3-(N-benzyl-N,N-dimethylammonium)propyl methacrylate chloride, 3-(N-benzyl-N,N-diethylammonium)propyl acrylate chloride, 3-(N-benzyl-N,N-diethylammonium)propyl methacrylate chloride, 3-(N-benzyl-N,N-dipropylammonium)propyl acrylate chloride and 3-(N-benzyl-N,N-dipropylammonium)propyl methacrylate chloride. Of course, the corresponding bromides and sulfates can also be used instead of said chlorides.

2-(N,N,N-Trimethylammonium)ethyl acrylate chloride, 2-(N,N,N-trimethylammonium)ethyl methacrylate chloride, 2-(N-benzyl-N,N-dimethylammonium)ethyl acrylate chloride and 2-(N-benzyl-N,N-dimethylammonium)ethyl methacrylate chloride are preferably used.

Mixtures of the abovementioned ethylenically unsaturated monomers can of course also be used.

All those free radical polymerization initiators which are capable of initiating a free radical aqueous emulsion polymerization are suitable for the preparation of the aqueous composite particle dispersion and of the aqueous polymer dispersion by free radical polymerization. In principle, these may be both peroxides and azo compounds. Redox initiator systems are of course also suitable. Peroxides which may be used in principle are inorganic peroxides, such as hydrogen peroxide or peroxodisulfates, such as the mono- or di-alkali metal or ammonium salts of peroxodisulfuric acid, for example the mono- and disodium or mono- and dipotassium or ammonium salts, or organic peroxides, such as alkyl hydroperoxides, for example tert-butyl, p-menthyl or cumyl hydroperoxide, and dialkyl or diaryl peroxides, such as di-tert-butyl or dicumyl peroxide. Azo compounds used are substantially 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and 2,2'-azobis(amidinopropyl) dihydrochloride (AIBA, corresponds to V-50 from Wako Chemicals). Suitable oxidizing agents for redox initiator systems are substantially the abovementioned peroxides. Sulfur compounds having a low oxidation state, such as alkali metal sulfites, for example potassium and/or sodium sulfite, alkali metal hydrogen sulfites, for example potassium and/or sodium hydrogen sulfide, alkali metal bisulfites, for example potassium and/or sodium metabisulfite, formaldehyde sulfoxylates, for example potassium and/or sodium formaldehyde sulfoxylate, alkali metal salts, especially potassium and/or sodium salts of aliphatic sulfinic acids and alkali metal hydrogen sulfides, for example potassium and/or sodium hydrogen sulfide, salts of polyvalent metals, such as iron(II) sulfate, iron(II) ammonium sulfate or iron(II) phosphate, enediols, such as dihydroxymaleic

acid, benzoin and/or ascorbic acid, and reducing saccharides, such as sorbose, glucose, fructose and/or dihydroxyacetone, may be used as corresponding reducing agents. As a rule, the amount of the free radical polymerization initiator used is from 0.1 to 5% by weight, based on the total amount of the monomer mixture.

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The entire range from 0 to 170°C is suitable as the reaction temperature for the free radical aqueous polymerization reaction in the presence or absence of the finely divided inorganic solid. As a rule, temperatures of from 50 to 120°C, frequently from 60 to 110°C, often from  $\geq 70$  to 100°C, are used. The free radical aqueous emulsion polymerization can be carried out at a pressure less than, equal to or greater than 1 bar (absolute), it being possible for the polymerization temperature to exceed 100°C and to be up to 170°C. Readily volatile monomers, such as ethylene, butadiene or vinyl chloride, are preferably polymerized under superatmospheric pressure. The pressure may be 1.2, 1.5, 2, 5, 10 or 15 bar or may also assume higher values. If emulsion polymerizations are carried out under reduced pressure, pressures of 950, frequently 900, often 850, mbar (absolute) are established. The free radical aqueous emulsion polymerization is advantageously carried out at 1 bar (absolute) under an inert gas atmosphere, for example under nitrogen or argon.

20 The aqueous reaction medium can in principle also comprise water-soluble organic solvents, such as methanol, ethanol, isopropanol, butanols, pentanols, acetone, etc. However, the polymerization reaction is preferably effected in the absence of said solvents.

25 In addition to the abovementioned components, free radical chain transfer compounds may optionally also be used in the processes for the preparation of the aqueous composite particle dispersion or the aqueous polymer dispersion, in order to reduce or control the molecular weight of the polymers obtainable by the polymerization.

30 Substantially aliphatic and/or araliphatic halogen compounds, for example n-butyl chloride, n-butyl bromide, n-butyl iodide, methylene chloride, ethylene chloride, chloroform, bromoform, bromotrichloromethane, dibromodichloromethane, carbon tetrachloride, carbon tetrabromide, benzyl chloride or benzyl bromide, organic thio compounds, such as primary, secondary or tertiary aliphatic thiols, for example ethanethiol, n-propanethiol, 2-propanethiol, n-butanethiol, 2-butanethiol, 2-methyl-2-propanethiol, n-pentanethiol, 2-pentanethiol, 3-pentanethiol, 2-methyl-2-butanethiol, 3-methyl-2-butanethiol, n-hexanethiol, 2-hexanethiol, 3-hexanethiol, 2-methyl-2-pentanethiol, 3-methyl-2-pentanethiol, 4-methyl-2-pentanethiol, 2-methyl-3-pentanethiol, 3-methyl-3-pentanethiol, 2-ethylbutanethiol, 2-ethyl-2-butanethiol, n-heptanethiol and its isomeric compounds, n-octanethiol and its isomeric compounds, n-nonanethiol and its isomeric compounds, n-decanethiol and its isomeric compounds, n-

undecanethiol and its isomeric compounds, n-dodecanethiol and its isomeric compounds, n-tridecanethiol and its isomeric compounds, substituted thiols, for example 2-hydroxyethanethiol, aromatic thiols, such as benzenethiol, ortho-, meta- or para-methylbenzenethiol, and all further sulfur compounds described in  
5 Polymerhandbook 3<sup>rd</sup> edition, 1989, J. Brandrup and E.H. Immergut, John Wiley & Sons, Section II, pages 133 to 141, but also aliphatic and/or aromatic aldehydes, such as acetaldehyde, propionaldehyde and/or benzaldehyde, unsaturated fatty acids, such as oleic acid, dienes having nonconjugated double bonds, such as divinylmethane or vinylcyclohexane, or hydrocarbons having readily abstractable hydrogen atoms, for  
10 example toluene, are used. However, it is also possible to use mixtures of the abovementioned free radical chain transfer compounds which do not interfere. The optionally used total amount of the free radical chain transfer compounds is as a rule  $\leq 5$ , often  $\leq 3$ , frequently  $\leq 1$ , % by weight, based on the total amount of the monomers to be polymerized.

15 The aqueous composite particle dispersions used according to the invention and the aqueous dispersions comprising aqueous polymer dispersion and finely divided inorganic solid usually have a total solids content of from 1 to 70, frequently from 5 to 65, often from 10 to 60, % by weight.

20 The composite particles or dispersion polymers used according to the invention have, as a rule, particle diameters of  $> 0$  and  $\leq 1\ 000$  nm, frequently  $\leq 500$  nm, often  $\leq 250$  nm. The determination of these particle diameters, too, is effected by the analytical ultracentrifuge method. The stated values correspond to the  $d_{50}$  values.

25 The composite particles which can be used according to the invention may have different structures. The composite particle may contain one or more of the finely divided solid particles. The finely divided solid particles may be completely surrounded by the polymer matrix. However, it is also possible for a part of the finely divided solid  
30 particles to be surrounded by the polymer matrix while another part is arranged on the surface of the polymer matrix. Of course, it is also possible for a major part of the finely divided solid particles to be bound on the surface of the polymer matrix.

35 It should also be stated that the aqueous composite particle dispersions can be dried in a simple manner to give redispersible composite particle powders (for example by freeze-drying or spray-drying). This is true in particular when the glass transition temperature of the polymer matrix of the composite particles obtainable according to the invention is  $\geq 50^{\circ}\text{C}$ , preferably  $\geq 60^{\circ}\text{C}$ , particularly preferably  $\geq 70^{\circ}\text{C}$ , very particularly preferably  $\geq 80^{\circ}\text{C}$ , especially preferably  $\geq 90^{\circ}\text{C}$  or  $\geq 100^{\circ}\text{C}$ . The composite  
40 particle powders are also suitable for the novel treatment of paper surfaces.

The mixtures of aqueous polymer dispersion and finely divided inorganic solid are obtained, for example, by stirring the corresponding amount of the finely divided inorganic solid, either in the form of powder or in the form of an aqueous solid dispersion, into an aqueous polymer dispersion stirred at from 20 to 25°C (room temperature) and mixing homogeneously.

In the novel treatment of the paper surface, the composite particles or the mixture of dispersion polymer and finely divided inorganic solid is or are applied to the paper surface in an amount of from 0.1 to 100, often from 0.2 to 20, frequently from 0.5 to 10, g/m<sup>2</sup> of paper. Larger amounts are also conceivable but as a rule are not economically expedient. If the composite particles or the mixture of dispersion polymer and finely divided inorganic solid is or are applied to the paper surface in the form of aqueous polymer dispersions, the abovementioned amounts are based on those amounts of composite particles or of mixture of dispersion polymer and finely divided inorganic solid which are contained in the aqueous dispersions. After the application of the aqueous dispersions, a drying step familiar to a person skilled in the art is as a rule carried out.

In particular, those composite particles or dispersion polymers whose polymers can be formed into films and whose minimum film formation temperature is  $\leq 150^{\circ}\text{C}$ , preferably  $\leq 100^{\circ}\text{C}$ , particularly preferably  $\leq 50^{\circ}\text{C}$ , are used for the novel process. Since the minimum film formation temperature is no longer measurable below  $0^{\circ}\text{C}$ , the lower limit of the minimum film formation temperature can be specified only by the glass transition temperature. The glass transition temperatures should not fall below  $-60^{\circ}\text{C}$ , preferably  $-30^{\circ}\text{C}$ . The determination of the minimum film formation temperature is effected according to DIN 53 787 or ISO 2115 and the determination of the glass transition temperature according to DIN 53 765 (differential scanning calorimetry, 20 K/min, midpoint measurement).

It may be advantageous if the paper coated with composite particles, particularly when coating is effected in the form of their aqueous dispersions, is subjected, after the coating process, to pressures and/or temperatures such that the polymer contained in the composite particles (process 1) forms a film. The same also applies if the paper surfaces are coated according to process 2 with an aqueous dispersion of a mixture of polymer and finely divided inorganic solid. Whether the drying conditions (temperature/pressure) are chosen so that the polymer forms a film, for example with the use of aqueous dispersions, or whether the film formation is effected in a downstream separate step is of no importance. When the corresponding aqueous dispersions are used, the film formation step frequently takes place during the drying.

The coated papers obtainable by the novel processes have a wide range of uses, for example as writing paper, newsprint, paper for journals, catalogs or books, as banknote paper, Bible paper, kraft paper, capacitor paper or photographic paper.

5

Advantageously, the novel papers can be written on and, for example, printed on by means of offset, flexographic and gravure printing processes. In particular the printed novel papers obtainable by the offset printing process have advantages with regard to their dry strength, wet picking resistance and ink absorption resistance and their good mottle properties.

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### Examples

#### I. Preparation of an aqueous composite particle dispersion

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416.6 g of Nyacol® 2040 and then a mixture of 2.5 g of methacrylic acid and 12 g of a 10% strength by weight aqueous solution of sodium hydroxide were introduced in the course of 5 minutes into a 2 l four-necked flask equipped with a reflux condenser, a thermometer, a mechanical stirrer and a metering apparatus, at from 20 to 25°C (room temperature) and 1 bar (absolute) under a nitrogen atmosphere and with stirring (200 revolutions per minute). A mixture of 10.4 g of a 20% strength by weight aqueous solution of the nonionic surfactant Lutensol® AT 18 (trade name of BASF AG, C<sub>16</sub>C<sub>18</sub>-fatty alcohol ethoxylate having on average 18 ethylene oxide units) and 61.4 g of demineralized water was then added to the stirred reaction mixture in the course of 15 minutes. 0.83 g of N-cetyl-N,N,N-trimethylammonium bromide (CTAB), dissolved in 200 g of demineralized water, was then metered into the reaction mixture in the course of 60 minutes. The reaction mixture was then heated to a reaction temperature of 80°C.

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At the same time, a monomer mixture consisting of 117.5 g of methyl methacrylate, 130 g of n-butyl acrylate and 0.5 g of methacryloyloxypropyltrimethoxysilane was prepared as feed 1 and an initiator solution consisting of 2.5 g of sodium peroxodisulfate, 11.5 g of a 10% strength by weight solution of sodium hydroxide and 100 g of demineralized water was prepared as feed 2.

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21.1 g of feed 1 and 57.1 g of feed 2 was then added via two separate feed lines in the course of 5 minutes to the reaction mixture stirred at the reaction temperature. The reaction mixture was then stirred for one hour at the reaction temperature. 0.92 g of a 45% strength by weight aqueous solution of Dowfax® 2A1 was then added to the reaction mixture. In the course of 2 hours, beginning at the same time, the remainders of feed 1 and feed 2 were then metered continuously into the reaction mixture.

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Thereafter, the reaction mixture was stirred for a further hour at reaction temperature and then cooled to room temperature.

5 The aqueous composite particle dispersion thus obtained had a solids content of 40.1% by weight, based on the total weight of the aqueous composite particle dispersion.

By dilution with demineralized water, the solids content of the aqueous composite particle dispersion was brought to 10% by weight at room temperature with stirring.

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## II. Testing of performance characteristics

For the investigation, wood-free base paper (basis weight 70 g/m<sup>2</sup>) from Scheufelen, Germany, was coated with 10 g/m<sup>2</sup> of a coating slip (calculated as solid), consisting of

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70 parts by weight of Hydrocarb<sup>®</sup> 90 (calcium carbonate from Omya AG, Switzerland),  
30 parts by weight of Amazon Plus<sup>®</sup> (kaolin from CADAM S.A, Brazil),  
0.15 part by weight of Polysalz<sup>®</sup> S (45% strength by weight aqueous solution of a  
20 polyacrylic acid sodium salt from BASF AG, Germany),  
10 parts by weight of Styronal<sup>®</sup> PR 8736 (50% strength by weight aqueous styrene/butadiene dispersion from BASF AG, Germany),  
0.3 part by weight of Sterocoll<sup>®</sup> FD (25% strength by weight aqueous ethyl acrylate/acrylic acid/methacrylic acid dispersion from BASF AG,  
25 Germany) and  
34 parts by weight of demineralized water,

by means of a DT Laboratory Coater from DT Paper Science Oy Ab, Finland at 30°C and atmospheric pressure (stiff blade having a thickness of 0.3 mm). The paper web  
30 was dried by means of an IR drying unit and air drying (8 IR lamps of 650 watt each, throughput speed 30 m/min).

Test strips measuring 35 cm x 20 cm were cut from the paper webs and were uniformly coated with the dilute aqueous composite particle dispersion. The amount of said  
35 dispersion was such that the amount of composite particles was 1.0 g/m<sup>2</sup> of paper surface. The test strips were then stored for 15 hours at 23°C and a relative humidity of 50% (DIN 50014-23/50-2). The test strips were then calendered by means of the table laboratory calender K8/2 from Kleinenewefers Anlagen GmbH, Germany, at room temperature. The nip pressure between the rolls was 200 kN/cm paper width and the  
40 speed was 10 m/min. The process was carried out four times altogether.

### Comparative example

- 5 The comparative example was carried out according to the abovementioned example, with the exception that the surface was not treated with the aqueous composite particle dispersion.

### Determination of the dry picking resistance using the IGT proof printer (IGT dry)

- 10 The test strips were printed at increasing speed in a printing unit (IGT printability tester AC2/AIC2) using a standard ink (printing ink 3808 from Lorilleux-Lefranc). The maximum printing speed was 200 cm/s. The ink was applied at a nip pressure of 350 N/cm.
- 15 The speed, in cm/sec, at which there were 10 picks from the paper coating slip (pick points) after the beginning of printing is stated as a measure of the dry picking resistance. The higher this printing speed at the tenth pick point, the better is the result rated.
- 20 Wet picking resistance

The test strips were produced and prepared as in the case of the testing of the dry picking resistance.

- 25 The printing unit (IGT printability tester AC2/AIC2) was set up in such a way that the test strips were moistened with water before the printing process.

The printing was carried out at a constant speed of 0.6 cm/s.

- 30 Picks from the paper are visible as unprinted areas. For the determination of the wet picking resistance, the ink density in comparison with a solid hue is therefore determined in % using a color densitometer. The higher the stated ink density, the better the wet picking resistance.
- 35 Picking resistance in the case of multiple printing (offset test)

The printing of the test strips [cf. testing of the dry picking resistance] was carried out at a constant speed of 1 m/s and at a nip pressure of 200 N/cm.

The printing process was repeated after 30 seconds. The number of passes until picking occurred is stated as the picking resistance. The larger the number of print processes until the first picking occurs, the better is the result rated.

5 Table 1: List of results

	Dry picking resistance in cm/s	Wet picking resistance %	Offset test Number
Example	71	57	6
Comparative example	63	51	4